

FORM PTO-1390 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

010482-US

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/009971

INTERNATIONAL APPLICATION NO.
PCT/DE00/01313INTERNATIONAL FILING DATE
26 April 2000PRIORITY DATE CLAIMED
30 April 1999

TITLE OF INVENTION

Method of Determining the Salt Content of a Liquid and Device for Practicing the Method

APPLICANT(S) FOR DO/EO/US

OHM, Klaus

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

a Post Card Receipt

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.101) 10/009971	INTERNATIONAL APPLICATION NO. PCT/DE00/01313	ATTORNEY'S DOCKET NUMBER 010482-US
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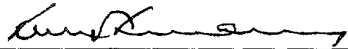
24. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO					
\$1040.00					
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO					
\$890.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO					
\$740.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)					
\$710.00					
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)					
\$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than _____ months from the earliest claimed priority date (37 CFR 1.492 (e)).					
<input type="checkbox"/> 20 <input type="checkbox"/> 30				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	19 - 20 =	0	x \$18.00	\$0.00	
Independent claims	2 - 3 =	0	x \$84.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$890.00	
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$445.00	
SUBTOTAL =				\$445.00	
Processing fee of \$130.00 for furnishing the English translation later than _____ months from the earliest claimed priority date (37 CFR 1.492 (f)).					
<input type="checkbox"/> 20 <input type="checkbox"/> 30 +				\$0.00	
TOTAL NATIONAL FEE =				\$445.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input checked="" type="checkbox"/> \$40.00	
TOTAL FEES ENCLOSED =				\$485.00	
				Amount to be: refunded	\$
				charged	\$

- a. ☒ A check in the amount of **\$485.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. _____. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Law Offices of Karl Hormann
 86 Sparks Street
 Cambridge MA 02138-2216



 SIGNATURE

Karl Hormann

 NAME

26,470

 REGISTRATION NUMBER

30 October 2001

 DATE

**VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY
STATUS (37 CFR 1.9(f) AND 1.27 (d)) - NONPROFIT ORGANIZATION**

Docket No.
010482

Serial No.

Filing Date

Patent No.

Issue Date

30 October 2001

Applicant/ **OHM, Klaus**
Patentee:

Invention: **Method of Determining the Salt Content of a Liquid and Device for Practicing the Method**

I hereby declare that I am an official empowered to act on behalf of the nonprofit organization identified below:

NAME OF ORGANIZATION: Stiftung Alfred-Wegener-Institut fuer Polar- und Meeresforschung

ADDRESS OF ORGANIZATION: Columbusstrasse
D-27568 Bremerhaven, Germany
TYPE OF NONPROFIT ORGANIZATION:

- ☐ University or other Institute of Higher Education
- ☐ Tax Exempt under Internal Revenue Service Code (26 U.S.C. 501(a) and 501(c)(3))
- ☐ Nonprofit Scientific or Educational under Statute of State of The United States of America
Name of State: _____ Citation of Statute: _____
- ☒ Would Qualify as Tax Exempt under Internal Revenue Service Code (26 U.S.C. 501(a) and 501(c)(3)) if Located in The United States of America
- ☐ Would Qualify as Nonprofit Scientific or Educational under Statute of State of The United States of America if Located in The United States of America
Name of State: _____ Citation of Statute: _____

I hereby declare that the above-identified nonprofit organization qualifies as a nonprofit organization as defined in 37 C.F.R. 1.9(e) for purposes of paying reduced fees to the United States Patent and Trademark Office regarding the invention described in:

- ☒ the specification to be filed herewith.
- ☐ the application identified above.
- ☐ the patent identified above.

I hereby declare that rights under contract or law have been conveyed to and remain with the nonprofit organization with regard to the above identified invention.

If the rights held by the above-identified nonprofit organization are not exclusive, each individual, concern or organization having rights to the invention is listed on the next page and no rights to the invention are held by any person, other than the inventor, who could not qualify as an independent inventor under 37 CFR 1.9(c) or by any concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

- ☒ no such person, concern or organization exists.
☐ each such person, concern or organization is listed below.

FULL NAME

ADDRESS

☐ 306-A Individual☐ Small Business Concern☐ Nonprofit Organization

FULL NAME

ADDRESS

☐ Individual☐ Small Business Concern☐ Nonprofit Organization

FULL NAME

ADDRESS

☐ Individual☐ Small Business Concern☐ Nonprofit Organization

FULL NAME

ADDRESS

☐ Individual☐ Small Business Concern☐ Nonprofit Organization

Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING:

Uwe Kersten

TITLE IN ORGANIZATION:

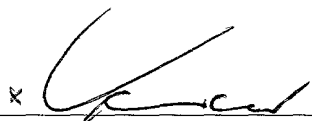
Manager of Technology Transfer

ADDRESS OF PERSON SIGNING:

Beuthener Str. 32
D-27578 Bremerhaven
Germany

SIGNATURE:

x



DATE:

09.10.2001
 9 October 2001

10/009971

JC05 Rec'd PCT/PTO 30 OCT 2001

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

International Application: PCT/DE00/01313
Filed 26 April 2000
Priority Claimed: 30 April 1999
Inventor: Ohm, Klaus
For: Method of Determining the Salt Content
of a Liquid and Device for Practicing
the Method

86 Sparks Street
Cambridge MA 02138-2216
30 October 2001

Hon.
Assistant Commissioner
for Patents
Washington DC 20231

Preliminary Amendment

Sir:

With a view to avoiding excess claims fees otherwise due, Applicant courteously requests that its claims as amended under Rule 66 PCT be amended as follows:

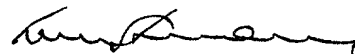
- Claim 1, line 1: change "Method" to --A method--;
- claim 2, line 1: change "Measuring" to --The--;
- claim 3, line 1: change "Measuring" to --The-- and "according to" to --of- and cancel "1 or";
- claim 4, line 1: change "Measuring" to --The-- and "according to at least one of claims 1 to" to --of--;
- claim 5, line 1: change "Measuring" to --The-- and "according to at least one of claims 1 to" to --of--;
- claim 6, line 1: change "Measuring" to --The-- and "according to at least one of claims 1 to" to --of--;
- claim 7, line 1: change "Measuring" to --The-- and "according to at least one of claims 1 to" to --of--;
- claim 8, line 1: change "Apparatus for practicing the method according to at

least one of claims" --An apparatus for--;
claim 8, line 2: cancel "1 to 8 of";
claim 9, line 1: change "Measuring" to --The--;
claim 10, line 1, change "Measuring" to "The" and "according to" to --of-- and
cancel "8 or";
claim 11, line 1: change "Measuring apparatus according to at least one of
claims 8 to 10" to --The apparatus of claim 10--;
claim 12, line 1: change "Measuring apparatus according to at least one of
claims 8 to 11" to --The apparatus of claim 11--;
claim 13, line 1: change "Measuring apparatus according to at least one of
claims 8 to 12" to --The apparatus of claim 12--;
claim 14, line 1: change "Measuring apparatus according to at least one of
claims 8 to 13" to --The apparatus of claim 13--;
claim 15, line 1: change "Measuring apparatus according to at least one of
claims 8 to 14" to --The apparatus of claim 14--;
claim 16, line 1: change "Measuring apparatus according to at least one of
claims 8 to 15" to --The apparatus of claim 15--;
claim 17, line 1: change "Measuring apparatus according to at least one of
claims 8 to 16" to --The apparatus of claim 16--;
claim 18, line 1: change "Measuring apparatus according to at least one of
claims 8 to 17" to --The apparatus of claim 17--; and
claim 19, line 1: change "Measuring apparatus according to at least one of
claims 8 to 18" to --The apparatus of claim 18--.

Remarks

A fresh copy of the claims amended as set forth hereinabove is
enclosed.

Respectfully submitted,



Karl Hormann
Registration No.: 26,470

Patent Claims

1. A method of determining the salinity of liquids by standard calibrated measurements of the electrical conductivity of a heated liquid sample in a measuring cell arranged in a constantly cooled and mechanically stirred as well as heatable water bath which is insulated to the exterior under control parametric consideration of the thermal conditions in the water bath characterized by the fact that the actual temperature (ϑ_B) is measured as an equivalent of the temperature (ϑ_P) of the sample with a high repetitive accuracy and inclusion of a maximum permissible lag error ($\Delta\vartheta_{\max}$) between the water bath and sample temperature (ϑ_B , ϑ_P) set by the required accuracy of determining the salinity (S), and that the control parameter for taking into account the thermal conditions is the time-wise drift ($\alpha = \Delta\vartheta_B/t$) of the temperature (ϑ_B) derivable from the temperature measurements, the permissible maximum value (α_{\max}) of which is defined as quotient ($\alpha_{\max} = \Delta\vartheta_{\max}/\tau$) of the maximum permissible lag error ($\Delta\vartheta_{\max}$) and a time constant (τ) of the measuring cell (MC) for a temperature equalization between the interior of the measuring cell and the water bath (WB), whereby the permissible maximum value of the time-wise drift (α_{\max}) of the temperature (ϑ_B) of the water bath is maintained by a low-lag and quickly controllable compensation of the heat currents (P_{\pm}) flowing into and out of the water bath (WB) to such a degree that the resulting quantity of the residual heat current (P_{rest}) does not exceed a predetermined maximum value (P_{restmax}).
2. The method of claim 1, characterized by the fact that the temperature (ϑ_B) of the water bath is maintained with the resultant residual heat current (P_{rest}) at the mean ambient temperature approximately

with a deviation of ± 1 K.

3. The method of claim 2,
characterized by the fact that

- 5 the energy input into the water bath (WB) by the stirring (P_R) is also utilized
for the quick and low-lag controllable heating (P_H) thereof.

4. The method of claim 3,
characterized by the fact that

- 10 the heat resistance (R) of the exterior insulation (I) of the water bath (WB) is
high.

5. The method of claim 4,
characterized by the fact that

- 15 the heat resistance (R) of the water bath cooling (PE) on the side of the bath
is high.

6. The method of claim 5,
characterized by the fact that

- 20 the temperature of the liquid sample (ϑ_P) is adjusted to the temperature (ϑ_B) of
the water bath in a separately controlled advance bath (PB).

7. The method of claim 6,
characterized by the fact that

- 25 the measuring sequence is carried out automatically by a computer (PC) and
that the salinity (S) of the liquid sample (PROBE) is calculated from the
measured values of temperature (ϑ_B) and conductivity (κ) on the basis of the
UNESCO formula.

- 30 8. An apparatus for determining the salinity of liquids by standard
calibrated measurements of the electrical conductivity of a heated liquid

sample which may be transferred from a sample vial into a measuring cell arranged in a water bath provided with a cooling, a stirring and a heating element as well as with a heat exchanger and provided at its wall with an external insulation and a control device in which the actual temperature (ϑ_b) of the water bath is measured with high repetitive accuracy and including a maximum permissible lag error ($\Delta\vartheta_{\max}$) between the water bath and sample temperature (ϑ_b , ϑ_p) determined by the accuracy demanded in by the determination of salinity (S) as the equivalent of the temperature (ϑ_p) of the sample and wherein the control parameter for taking into account the thermal conditions is the time-wise drift ($\alpha = \Delta\vartheta_B/t$) of the temperature (ϑ_b) of the water bath the permissible maximum value (α_{\max}) of which is defined as quotient ($\alpha = \Delta\vartheta_{\max}/\tau$) of the maximum permissible lag error ($\Delta\vartheta_{\max}$) and a time constant (τ) of the measuring cell (MC) for a temperature balancing between the interior of the measuring cell and the water bath (WB), whereby the permissible maximum value of the time-wise drift (α_{\max}) of the temperature (ϑ_b) of the water bath is maintained to such a degree by a low-lag and quick controllable adjustment of the heat currents (P_{\pm}) flowing into and out of the water bath (WB) that the quantity of the resulting residual heat current (P_{rest}) does not exceed a corresponding predetermined maximum value (P_{restmax}), whereby for the direct measurement of the actual temperature ($\Delta\vartheta_B$) of the water bath there is provided in the water bath a precision thermometer (TM) having a long term stability of less than 1 K per year and a time constant of less the .5 s.

9. The apparatus of claim 8, characterized by the fact that the precision thermometer (TM) is provided with temperature dependent semiconductor resistors.

10. The apparatus of claim 9, characterized by the fact that

the stirrer provided for stirring and heating the water bath (WB) is structured as a rotationally controllable stirring propeller (Q) having a stirring vane (SP) similar to a ship's screw of high hydrodynamic efficiency which is drivable by a continuously controllable electric motor (EM) arranged at the exterior of the
5 water bath (WB).

11. The apparatus of claim 10,
characterized by the fact that
that in the wall of the water bath (WB) there is arranged at least one Peltier
10 element (PE) provided with a thermal insulation (I) at the cooling side of the
water bath (WB).

12. The apparatus of claim 11,
characterized by the fact that
15 the measuring cell (MC) has a volume in the range of 2 ml and is provided
with strip electrodes (SE).

13. The apparatus of claim 12,
characterized by the fact that
20 that for heating the liquid sample (PROBE) there is provided a separate
controllable advance bath (PB) provided with a preheat exchanger (PWT).

14. The apparatus of claim 13,
characterized by the fact that
25 for carrying out standard calibrations and measurements there is provided a
four-way valve (FV) provided with inputs to a vial (A) of standard sea water
(SSW), to a bottle (B) of sample water (PROBE) as well as to a cleaning and
an air conduit (H₂O, Air).

30 15. The apparatus of claim 14,
characterized by the fact that

for evacuating the measuring cell (MC) there is provided a diaphragm pump (MP).

16. The apparatus of claim 15,
5 characterized by the fact that
for filling the measuring cell (MC) there is provided a dosage pump (DP).

17. The apparatus of claim 16,
characterized by the fact that
10 a computer (PC) is provided for regulating the water bath, controlling the
measuring sequence, and storing results.

18. The apparatus of claim 17,
characterized by the fact that
15 that the conductivity measurement of the liquid sample (PROBE) is carried
out at a fully automatically balancing precision bridge.

19. The apparatus of claim 18,
characterized by the fact that
20 there is provided an indicator of satisfied measuring conditions.

25

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3/PRTS

10/009971
JC05 Rec'd F327TC 3 0 OCT 2001

Method of Determining the Salt Content of Liquids and
Device for Practicing the Method

5 Description

- The invention relates to a method of determining the salinity of liquids by standard calibrated measurements of the electrical conductivity of a liquid sample of predetermined temperature in a measuring cell arranged within a cooled and mechanically stirred as well as heatable water bath which is insulated to the outside, under controlled parametric consideration of the thermal conditions in the water bath, and to a device for practicing the method.
- 15 State parameters in the thermodynamic sense unequivocally define the state of a liquid. Taking sea water in particular as a well-defined liquid, three state parameters are sufficient for the definition; all other parameters may be derived therefrom. The set of parameters of temperature, salinity and pressure are considered by classical oceanography as the simplest and most
- 20 precisely measurable state parameters. Since about 1960 it has been possible by using electrical sensors continuously to measure *in situ* electrical conductivity, temperature and pressure of the sea. Instead of the classical parameter "salinity", "electrical conductivity" is included in the set of the three measured characteristic values defining the state of sea water, because it can
- 25 be measured more easily *in situ* and may be converted into salinity by means of an empirical normalized formula. Therefore, even though nowadays the salinity would no longer be required to define the fluid density, one would have to have recourse to it to understand oceanic processes. As a conservative value, the salinity remains constant at changes in temperature
- 30 and pressure, and it is also not affected by the metabolism of plants and animals living in the sea. It is subject to simple rules resulting from the preservation of the water and salt masses, when sea water of different

salinities is mixed. For that reason, the salinity is ideally suited for characterizing bodies of water and as a tracer for examining large volume currents. But the knowledge of given salinity may also be important in other fluids, such as, for instance, pharmaceutical chemistry or food analyses.

5

Various methods and apparatus for defining the salinity of fluids are known in the prior art. Japanese patent JP 63111457 (1988) discloses a method by which the salinity is determined on the basis of the parameters of temperature, pressure and speed of sound. To this end, ultra-sonic

10 measuring paths are positioned in a submarine area and the time lag between transmitter and receiver of oscillator-generated sinusoidal ultrasound signals is registered.

Japanese Patent JP 60161554 (1985) discloses another method of carrying

15 out *in situ* measurements of salinity in sea water, in which a coil of appropriate winding diameter and length is lowered into the sea in a non-magnetic, non-metallic and waterproof container and is charged with an alternate voltage. The magnetic flux then permeates the surrounding sea water. The conductivity and, hence, the level of the induction current through

20 the water is defined by the salinity. The induction current in the water generates a counter induction in the coil which weakens the current in the coil. The measured coil current is then a direct value of the salinity of the sea water. The indicated method was introduced as early as 1957 in the paper

"Gerät zur Schnellregistrierung in der Ozeanographie" (Apparatus for Rapid

25 Registration in Oceanography) by H. Hinkelmann (Z. f. angewandte Physik einschl. Nukleonik, Volume IX, H10, pp. 505-513). The sea water resistance is used as an arm of an almost balanced alternate current bridge. By a

complex bridge resistance, a phase angle which depends upon the sea water resistance is generated between the input and output voltages. This phase

30 angle defines the frequency of an oscillator containing the alternate current bridge. The corresponding apparatus to carry out the two methods are laboratory devices for the calibration of *in situ*

devices. More detailed descriptions relating to these apparatus may be found in the papers "A conductivity bridge for measurement of the salinity of sea-water" (1956, Schleicher, Bradshaw, Journal Conseil Permanent International pour l'Exploration de la Mer, Volume 22, pp. 9-20); "A modification of the
 5 Werner-Smith-Soule salinity bridge for the determination of salinity in sea water with details of construction, operation and maintenance (Paquette, 1958, Univ. Of Washington, Department of Oceanography, Technical Report No. 54-14, pp. 1-57); "A new automated laboratory salinometer" (1975, Dauphinee, Klein, Sea Technology, Volume 16, pp. 23-25) or "Progress in the
 10 measurement of salinity and oxygen at the Woods hole Oceanographic Institution" (1987, Knapp, Stalcup, Technical Report, WHOI-87-4, Woods Hole Oceanographic Institution, pp. 27 seq.).

Japanese Patent JP 62085852 (1987) describes a method of
 15 measuring the salinity in liquids the temperature of which differs from a reference temperature. To this end, the measured conductivity voltage is divided by a temperature-dependent compensation voltage. In the apparatus known from the paper "An inductive salinometer" by Brown and Hamon (1961, Deep-Sea-Research, Volume 8, pp. 65-71) the temperature
 20 dependence is balanced by NTC (negative temperature coefficient) - thermistors.

A method of determining salinity is known from Canadian Patent CA 1,199,367 or its corresponding American patent US 4,511,845, which is
 25 based upon defining a rate of conductivity of sample water relative to standard sea water. The essential contents of these patents has also been published in the prospectus "Laboratory Salinometer - Autosol - Model 8400 A" of Guildline Instruments, Ltd., P.O.Box 99, Smith Falls, Ontario, K7A 4S9, Canada. The invention proceeds from this prospectus as the closest state of
 30 the art. Since this is, however, merely an apparatus pamphlet, the basic measurement method which has also been described in the patents will first be described.

The principle of the method of the Autosal (AS) 8400 is that the electrical conductivity of a sea water sample is measured after the form factor of the measuring cell and the sample temperature of sea water has been implicitly defined as normal. This assumes that the form factor and the

5 temperature will remain constant until a following standardization. The ratio of the conductivity of a sample of sea water is defined at a predetermined temperature relative to a sample of standard sea water. The salinity is calculated in accordance with the "Praktische Salzgehaltsskala of 1978" (Practical Salinity Scale of 1978). The temperature term of this formula

10 affects the result of the salinity calculation insignificantly, so that the actual temperature during the measurement need not be known precisely. It is, however, important that the temperature present at standardization remain stable. As the conductivity of sea water is strongly dependent upon temperature every temperature drift fully affects the result. For the intended

15 accuracy of the salinity measurement the temperature between two standardizations must for this reason be kept constant with great accuracy. In order to attain this constancy, which puts great demands on the temperature control and upon the maintenance of ambient conditions, the method of operation for attaining the best possible accuracy should settle

20 over the course of four days at least. The same applies following every disturbance in the operating sequence, for instance, by mistakes in the manual operation. In order for the water of the sample attaining the same temperature as the water bath, the sample is conducted through a metal capillary positioned in the water bath, the capillary functioning as a heat

25 exchanger. Where as a result of too great a difference in temperatures, the heat exchanger is incapable of bringing about full temperature equalization, the second condition is not met. In case of a deviating sample temperature the heat exchanger transmits heats to the bath which may lead to a change in temperature which may exceed permissible tolerances.

30

Operational experience with the measuring method realized with the AS 8400 has shown that even sample temperature differences permitted by

the manufacturer may lead to impermissible temperature changes of the water bath. Any occurring malfunctions cannot be satisfactorily counteracted. In order to take accurate measurements, it is thus necessary to practice the known measuring method in a highly constant climatized room of the kind for purposes of field tests are available only on few research ships. In the case of ships which have no such complex laboratory equipment the samples must, therefore, be examined in institute (home-based) laboratories.

However, the usual storage times of at least four weeks until the ship returns to its home base, the sample may suffer from significant changes. In summary, the known method and the apparatus for practicing it are subject to too great a dependence upon the ambient and operating conditions and upon the operating person.

The problem upon which the present invention is based is thus to be seen in avoiding the difficulties arising in connection with the known method and additionally markedly to improve a corresponding apparatus for practicing the method by a number of suitable technical measures. The aim of the invention is to provide improved measuring precision by a simple and safe operation. Furthermore, consideration is also to be given to automation and economy.

In the method in accordance with the invention, the problem is solved by the actual temperature of the water bath being measured with high repetitive precision as an equivalent for the sample temperature, taking into consideration a maximum permissible lag error between the temperature of the water bath and the sample as demanded by the accuracy of the salinity measurement and the control parameters for considering the thermal conditions derivable from the drift in time of the temperature of the water bath, the maximum value of which is defined as the quotient of the maximum permissible lag error and a time constant of the measuring cell for balancing the temperature between the interior of the cell and the water bath.

The method in accordance with the invention dispenses with keeping constant the temperature of the water bath to accommodate the thermal conditions in the water bath, the control of which is extremely difficult primarily because of time lags occurring in the control loop. The temperature of the water bath may now adjust itself in accordance with untouched ambient conditions. In case of changes, the rate of change only has to stay within predetermined limits, otherwise a balance control will intervene. For this reason, the method may be practiced in a normal laboratory. The actual water bath temperatures are measured at a high repetitive accuracy, i.e. at a high resolution, and are put in relation, as control parameters, with the registered interval between individual measurements or for purposes of a standard calibration to determine the drift in temperature over time. The standard calibration is based upon the actual values of the actually used standard sea water sample, and allowances are made for possible calibration errors of the temperature sensor. Accordingly, to define the salinity of the liquid sample the indicated temperature of the water bath may be used without further consideration of any measuring error of the temperature sensor.

The basic condition for this approach is the assumption of equivalence between the sample temperature ϑ_{p1} relevant to the salinity of the liquid sample liquid and the water bath temperature ϑ_B which can be measured without substantial influence. The sample temperature ϑ_{p1} cannot, however, be sufficiently accurately measured in the measuring cell without impermissibly impeding the measurement of the conductivity. In this connection, the term "equivalency" is to connote that the equality between the sample temperature ϑ_p and the water bath temperature ϑ_B is postulated only up to a permissible difference. This permissible difference is, in fact, a "lag error" $\Delta\vartheta = \vartheta_B - \vartheta_p$ which is caused by the fact that bath and sample have not at once the same temperature when the bath temperature ϑ_B changes. Its maximum permissible value is determined as "maximum permissible lag error" $\Delta\vartheta_{\max}$ as a function of the desired accuracy of the result of the salinity.

In the first CTD measurements the accuracy of the temperature measurement was in the range of 10 mK. However, more precise measurements were made possible as a result of progress in the measuring technique. These became mandatory as oceanographers focussed on polar regions. There, the present range of values is strongly reduced relative to the main ocean, and the range in the vicinity of the freezing point of water in particular is relevant so that a correspondingly higher measurement accuracy in the range of 1 mK should be aimed at. In order to achieve it, improved measurement processes and components immune from cross currents (transverse influences) are required as are reproducible calibration processes and more stable standards. The largest permissible error aimed at nowadays, should be below 10^{-3} in the salinity the measurement of which has no unit. This corresponds to a maximum relative error of $3 \cdot 10^{-5}$. To this end the temperature or lag error must be less than 1 mK.

In the method in accordance with the invention the regulation aims at balancing the positive and negative heat currents into the water bath so that its temperature change in time remains less than a predetermined limit value "maximum permissible drift" α_{\max} . If it is attained or exceeded the measurements will stop. The control of a resulting heat current is simpler than the control of a rigidly determined temperature maintained within narrow limits, and it achieves its goal substantially faster than the latter. The control unit us need now only recognize a temperature drift and, except for a permissible residual error, reduce the sum of the heat currents to zero. A change in ambient conditions now no longer necessitates immediate action by the control which is also important as to the measuring frequency and evaluation.

To prove the accuracy of the assumption of equivalence of water bath and sample temperature and for defining limit values and numeric examples for the values set forth supra reference is made to the end of the general

description.

An apparatus for practicing the invention is closely connected to the method in accordance with the invention and the principles practiced. In order clearly to set forth these connections, including different embodiments, and the differences relative to the prior art, and in order to prevent repetitions, a preferred apparatus in accordance with the invention for practicing the method in accordance with the invention will initially be explained in greater detail.

10 The prior art upon which the invention is based for realizing a corresponding measuring apparatus is constituted by the generally acknowledged standard apparatus "Autosal (AS) 8400" referred to supra, of the Guideline company. This is an apparatus in which a liquid of predetermined temperature can be transferred from a sample bottle to a
15 measuring cell arranged in a water bath equipped with a means for cooling, stirring and heating as well as with a heat exchanger, and which at its wall is provided with an exterior insulation, and which is provided with a control unit for adjusting the thermal conditions in the water bath. Further explanations of details of the known apparatus will be given in connection with corresponding
20 embodiments of the invention.

With a view to distinguishing the apparatus in accordance with the invention from the known apparatus, the name "conductivity- reference- measuring-place" (LRM) has been chosen for the former. At the time the AS
25 8400 was conceived, thermometers with long-time measuring errors smaller than .3 mK were exceedingly expensive. For that reason, the known measuring method aimed to maintain a temperature constant rather than to measure it. Modern requirements, however, are no longer satisfied by a constant temperature of the bath; this technology is substantially exhausted
30 whereas the present invention is capable of meeting substantially higher specifications.

The decisive improvement of the method in accordance with the invention is the fact that the temperature is no longer maintained constant; rather, its permissible change is measured taking into account the maximum permissible lag error. Errors of the thermometer used resulting from

5 insufficient calibration or long-term drift are arrested by the standardization, so that the temperature of the water bath is measured directly. In terms of a device for practicing the inventive method, the solution to the problem referred to supra may be seen in a precision thermometer having a long-time drift of less than 1 mK per year and a time constant below .5 s. The precision

10 thermometer may be provided with platinum resistors, for instance, and preferably, in a further embodiment of the invention, is provided with temperature immune semiconductor resistors. Such thermometers are extremely robust and insensitive to shock yet highly accurate. The semiconductor resistors are so-called "hot conductors" (NTC thermistors) the

15 resistance values of which decrease with increasing temperatures. A temperature selection dial of the kind provided, for instance, in the known AS 8400 for fine-tuning one of several different temperatures, is not required for the inventive LRM.

20 In the method according to the invention, the control is realized in a control circuit in which the balanced heat currents constitute the control parameter and a corresponding heat current constitutes the setting parameter. In accordance with an improved embodiment of the inventive method it is advantageous to maintain the maximum permissible value of the

25 drift over time of the water bath temperature by a low-delay and rapid balancing of the heat currents flowing into and out of the water bath such that the resultant value of the heat current does not exceed a predetermined maximum. Control of the residual heat current P_{ges} composed of the heat current components for cooling P_K , heating P_H , ambience P_I , stirring P_R ,

30 sample P_P , measuring P_M and illumination P_B may be easily provided, and deviations may be quickly and simply compensated. Details of individual components have been described at the end of the general description.

In accordance with a further embodiment, in this kind of residual heat control it is reasonable to maintain the bath temperature ϑ_B at an approximate deviation of ± 1 K at the mean temperature ϑ_L by means of the resulting residual heat current P_{ges} . This leads to low heat currents because of the insulation of the water bath. The goal is to use the ambient temperature ϑ_L as the input for controlling the process sequence. The ambient temperature may occur automatically without complex measures such as, for instance, providing thermostats. All control and adjustment processes are thus based on a sure but simple support.

If it is assumed that the heat current P_K extracted from the water bath by constant cooling is constant and the other heat currents are difficult to affect or negligible, heat balancing in accordance with the invention may in the simplest manner be adjusted by changing the heat current P_H by controlled heating. By means of a mean heat output P_{hm} , the sum of the heat currents P_{ges} may be controlled to zero since the permissible temperature drift α_{max} is not exceeded.

In accordance with a further embodiment of the invention it is of particular advantage also to utilize the input of energy into the water bath by stirring for rapid and low-delay controllable heating. To this end, in an advantageous embodiment of the apparatus, the stirrer for stirring and heating the water bath may be a rotation-controllable stirring propeller similar to a ship's propeller of high efficiency which may be driving by a continuously controllable electric motor arranged outside of the water bath.

Heating of the water bath is carried out by the stirrer by conversion of mechanical energy into thermal energy so that the cooling output P_K must be compensated by the stirring output P_R and the heating output P_H is eliminated as an independent value. It is reasonable to select a cooling output which is equal to the sum of the minimum stirring power necessary to ensure minimum intermixing in the water bath and of the amplitude of the two varying heat

currents. Heating of the water bath is accomplished by utilizing the frictional heat of the stirrer which is added proportionally to the water bath. Since heat is generated at the exterior of the stirrer and in the water by internal friction and since the heated water is distributed directly by the stirrer, a greater
5 degree of distribution is now achieved with practically no time delay in view of the fact that there is no longer any heat capacity and no heat resistance of an additional heating element. For this purpose, a good hydrodynamic efficiency of the stirring wing is advantageous.

10 The ship's propeller used to this end as well as the kinetic energy of the water provide for the rapid and homogenous distribution in the bath of the energy converted at the stirrer to heat. Additional heat input from the heat of the motor is prevented by arranging the electric motor outside of the water bath. Such electric motors, as well as, for instance, electrically commutated
15 direct current motors, are simple and robust. Control of their rotations is accomplished with low lag and quickly. In the known apparatus AS 8400 the constant temperature of the water bath is set at a great time delay by two heat lamps using thick-walled glass cylinders as sources of heat and controlled by two NTC sensors and a dual point control. For that reason, the
20 heat lamps may be viewed as an unfavorable structural element for the control of temperature.

In the known AS 8400 the continuously running cooling of the water bath is performed by a Peltier element provided with an air heat exchanger at
25 the warm side. Such a cooling has a relatively low heat resistance and is very sensitive to external temperature changes. For that reason, another embodiment of the method in accordance with the invention provides for a high heat resistance of the external insulation. To that end the apparatus in accordance with the invention is advantageously provided with at least one
30 Peltier element in the wall of the water bath which at the cooling side provides for a thermal insulation in the water bath. Owing to the high heat resistance the heat current P_i is limited by the exterior skin of the water bath. An

analysis of the bath insulation has shown, however, that it is of little use simply to increase the wall thickness of the insulation because of the heat resistance of the insulated wall being positioned in parallel to that of the water bath cooling. The latter is composed of the resistance of the Peltier element
5 which in the usual size has a heat resistance of 1 K/W, and of the resistance of heat exchangers connected in series therewith. At the surrounding side the heat exchanger usually has a very low resistance. Therefore, changes in temperature in the vicinity bring about very strong changes in the heat flow into the bath which may result in impermissible temperature changes. By this
10 way of low heat resistance the effect, therefore, remains largely independent of the remaining insulation of the bath.

In general, the heat exchangers at the side of the bath are connected with the lowest possible heat resistance to the Peltier element. In order to
15 achieve as great an effectiveness of the cooling element as possible. In accordance with an advantageous further embodiment of the invention the heat resistance of the water bath cooling at the side of the bath is high in order further to improve the heat resistance of the water bath relative to its environment. Therefore, an insulation is deliberately provided, the reason for
20 it being that a predetermined heat flow over a small heat resistance is obtained by a correspondingly low temperature difference. If the same heat flow is to be obtained over a greater heat resistance which provides improved insulation of the bath from the environment, the temperature difference has to be increased which is to say that the cold side has to be operated at a lower
25 temperature. If the room temperature then changes by a predetermined value, the temperature at the cold side will change by about the same value. But in the case of a high heat resistance the change in the relative temperature difference is less than in the case of a low heat resistance. The heat flow will change correspondingly less, there will be less disturbance of
30 the bath at the same change in temperature of the environment as is the case in the known operation. That, of course, the aim of the embodiments. An additionally improved external insulation can only augment this effect.

However, the useful heat pumping capacity (product of the pumped heat flow and the temperature difference improve above the cooling element) is then reduced by the greater return heat flow. This may be compensated, for instance, by parallel operation of two cooling elements. For improved clarity,
5 a numeric example for explaining these concepts has been set forth at the end of the general description, where relevant values, interconnections and formulae as well as numeric examples have been explained in greater detail.

10 In the method known from the prior art, the samples and the standard sea water are stored, for raising them to the same bath temperature, in the same room during the input process. In the actual operating process, the samples are adjusted in a heat exchanger in the water bath to the temperature of the bath. At common temperature differences between bath and sample this is carried out with adequate accuracy. However, the heat
15 quantity which at deviating temperatures is carried into the bath with the sample must not be ignored. It is in the rough field operation where greater temperature differences cannot be avoided. For that reason, it is advantageous in a further embodiment of the method in accordance with the invention to adjust the temperature of the liquid sample to the temperature of
20 the water bath in a separately controlled advance bath. It is also possible quickly and highly precisely to perform measurements of fresh samples in the advance bath without long delays for compensating measures. The large heat exchanger in the water bath is divided, and a portion of it is arranged in a small advance bath the temperature of which may be adjusted to the
25 temperature of the bath with a maximum deviation of $\pm .3$ K. Samples may then be processed the temperature of which may differ from the temperature of the bath up to the range of 4 K. When exiting from this advance bath the sample will have discharged almost its entire excess energy, and in the second portion of the heat exchanger in the water bath it will be adjusted
30 precisely to the temperature of the bath without any significant flow of energy. The demands on the control may be easily satisfied. The advance bath is provided with a cooling element of low heat resistance as it need not be

especially well insulated from the environment. At the low required control precision and the low required efficiency the cooling element may also be used for heating by flow reversal.

5 In order further to improve the known method a further embodiment of the invention provides for an automatic and computer-controlled measuring operation and for calculating the salinity of the liquid sample on the basis of the measured values for temperature and conductivity in accordance with the UNESCO formula. As a result, the temporal measuring operation is more
10 substantially and more uniformly determined by the apparatus which improves the quality of the measurements. Errors in the operation of the apparatus and in the operating sequence may be substantially avoided. The reproducibility of the results of the measurements is improved. It is possible more economically to utilize the required apparatus in a permanent operation
15 as monitoring and operating requires attention at reduced concentration.

An important value in connection with the heat flow balance of the water bath is the heat input by the sample itself. With the known AS 8400, there is no advance heating, and the volume of the measuring cell is about 15
20 ml. Continuous sequences of measurements with continually new fillings of the measuring cell lead to corresponding disturbances of the temperature of the water bath and, hence, to extended balancing times. For that reason, it is better to provide a measuring cell of a volume of about 2 ml and strip electrodes, as is the case in a further embodiment of the apparatus in
25 accordance with the invention. Such a small volume, because of the small ratio of its volume relative to the water bath allows for a greater difference in temperature relative thereto. This means a further simplification of the pre-heating of the sample and an improvement in the processing rate. Instead of the known glass channels in the measuring electrode for the electrodes the
30 apparatus in accordance with the invention utilizes simple strip electrodes applied and baked by a platinum paste.

The possibility of preheating the sample in accordance with the invention may be realized, according to a further embodiment of the invention, by providing a separate controllable advance bath provided with a heat exchanger for heating the liquid sample. Such an advance bath, having a
5 volume, for instance, of .5 l is of very simple construction and may be integrated into the LRM without any difficulties. Cooling is provided in a known fashion by a Peltier element in particular. Heating may be accomplished by the cooling element by flow reversal thus making use of the heat exchanger for cooling as well as for heating.

10

At the beginning and at the end of the measuring sequence, but at least twice daily, the known AS 8400 is standardized. For this purpose a vial of standard sea water is shaken, opened and connected to the sample suction hose. The measuring cell is then filled by means of a peristaltik
15 pump. The measuring cell may be observed through a window in order to prevent interfering air bubbles and to shut down the pump before the sample water reaches and plugs up the vent capillaries. For emptying the measuring cell one closes with one's finger an air hole in the front plate through which pressurized air escapes from the measuring cell. This leads to the generation
20 of higher air pressure over the sample water in the measuring cell for pressing the sample water out of the cell by way of a siphon, thus emptying the measuring cell. The peristaltic pump still remains filled with sea water, however. This filling and emptying is repeated several times.

25 According to a further embodiment, the LRM is provided, for carrying out standard calibrations and measurements, with a four-way valve having channels leading to a vial of standard sea water, to a bottle of sample water as well as to a cleaning and air channel. Such a four-way valve allows simple selection between connected media. The measuring cell is evacuated by way
30 of a capillary protected from plugging up; the cell may be automatically filled by simple actuation of the four-way valve. For evacuating the sample liquid following a measurement it is advantageous in accordance with a further

embodiment to provide a diaphragm pump. This diaphragm, pump which may be of small dimensions, will generate pressurized air only when the cell vent is connected to the diaphragm pump by way of a simple two-way valve. By separating the air currents, pressurized air need be generated only when it is needed. When changing samples during rinsing the entire system including the pump is evacuated; the sample water is thus more thoroughly changed and measurement errors are reduced.

Heretofore, the use of a peristaltic pump has required visual inspection of the filling state of the measuring cell. The ability automatically completely to fill the measuring cell is an important step toward automation of the measurements. For that reason it is advantageous to provide, as proposed by a further embodiment of the invention, a dosage pump which requires no observation while the measuring cell is being filled. This may be a peristaltic pump in view of the fact that with the LRM venting is no longer as sensitive as it is with the known AS 8400; the measuring cell is no longer damaged if it is slightly overfilled. The use of an optical level sensor is also possible.

Several measures may be realized in connection with the LRM in accordance with the invention to bring about further improvements, such as, in particular, providing a personal computer for regulating the water bath, for controlling the measuring sequence and for storing the results of measurements; conducting the measurement of the conductivity of the sample liquid with a fully automatically balancing precision bridge; and providing an indicator to show satisfaction of the measuring conditions. In the known AS 8400 the setting, balancing and standardizing operations are performed manually by appropriate devices, buttons and potentiometers. No Potentiometers are provided in the LRM. The so-called K_{15} -value of the standard sea water vial is input only once and three sufficiently conforming measurements are taken of the conductivity of the standard sea water. The K_{15} -value connotes the conductivity ratio at 15°C and normal pressure of a predetermined solution of potassium chloride the concentration of which is set

(2) $T_B = \alpha t + T_0$

wherein $\alpha = \frac{dT_B}{dt}$ → change over time of the bath temperature: drift

5 T_0 → temperature of the bath at time t_0

It is a precondition of the equivalence calculation the time-wise behavior of the measuring cell and of the thermometer may be represented as a first order differential equation

10

(3) $T_M = T_M \frac{dT_M}{dt} = \alpha t + T_0$

wherein $\tau_M = R_T \cdot C_T$ → time constant of the thermometer

T_M → measured temperature

15 R_T → thermal resistance water bath - thermometer

C_T → heat capacity of the thermometer

The differential equation, by adding a term for the calibration error, is solved as

20

(4) $T_M = T_0 + \alpha t - \alpha \tau_M \left(1 - e^{-\frac{t}{\tau_M}} \right) + \Delta T_M$

wherein ΔT_M → calibration error

25 For times $t \gg \tau_M$ equals $T_M = T_B - \alpha \tau_M$

The largest deviation between thermometer and the temperature of the measuring cell is

(5) $T_M - T_{MC} = \alpha(\tau_M - \tau_{MC}) + \Delta T_M$

30 wherein T_{MC} → temperature of the measuring cell

τ_{MC} → time constant of the measuring cell

The time-wise course of the difference of the temperatures of the thermometer and measuring cell is

$$(6) \quad T_M - T_{MC} = \alpha \left[\tau_M \left(1 - e^{-\frac{t_1}{\tau_{MC}}} \right) \right] + \Delta T_M$$

5

wherein $t_1 \rightarrow$ measuring time 1

The expression between brackets is always between 0 and 1.

The increase in water temperature be assumed to be at just

$$10 \quad \alpha_{max} = \frac{\alpha}{1 - e^{-\frac{t_1}{\tau_M}}}$$

with a denominator always ≤ 1 results in $\alpha_{max} \leq \alpha$

and substituted in (6)

$$15 \quad (7) \quad T_M - T_{MC} = \alpha_{max} \left[\tau_M - \tau_{MC} \frac{1 - e^{-\frac{t_1}{\tau_{MC}}}}{1 - e^{-\frac{t_1}{\tau_M}}} \right] + \Delta T_M$$

20

Since the time constant of the measuring cell is greater than that of the thermometer by a factor of about 100, with $\tau_{MC} > \tau_M$ the denominator of the fraction is always smaller than the numerator so that the temperature difference always remains below the highest permissible limit from (5). The equivalence precondition of the temperatures between sample and water bath

25 has thus been demonstrated.

In the example, the temperature of the water bath increased more quickly than postulated by α_{max} , but the indication of the quicker thermometer initially does not exceed this limit value and the measurement by the slower

30 measuring cell will, therefore, not be disturbed. Only if this condition lasts for an extended period, the thermometer and, in the end, the measuring cell as well will reveal an impermissible temperature increase. Upon reversal of the drift conditions it will, of course, be necessary, following indication of

permissible conditions by the thermometer, to wait for a definable time until measuring conditions of the measuring cell have also been restored. In automatic measurements, the controlling computer will detect the maintenance of the measuring conditions.

5

II) Lag Error, Temperature Drift

An increase in the temperature ϑ_B of the water bath under the influence of temporally constant set value always follows a linear time path (analogously to capacitive control circuits with set values of current and voltage). The time constant of the measuring sensor (.1s) usually is very small and may be ignored by comparison with a time constant τ of the measuring cell, which in the AS 8400 is in the range of 28 s, even if a measured value is recorded, for instance, at intervals of 2 s only. The time constant τ denotes the product of heat resistance of the glass body of the measuring cell and the heat capacity of the filled-in sample. As time lag it is measure of the longest permissible time interval between filling of the measuring cell and the first temperature measurement and constitutes a characteristic of the filled measuring cell and is experimentally defined during manufacture of the apparatus.

The lag error may be calculated from

$$\Delta\vartheta = (d\vartheta_B / dt) \cdot \tau$$

From this, the temperature drift may be derived as

$$\alpha = d\vartheta_B / dt = \Delta\vartheta / \tau$$

If, given the preconditions set forth supra, a maximum permissible lag error of the measuring cell is postulated as $\Delta\vartheta_{\max} = .3 \text{ mK}$ at a time constant of $\tau = 28 \text{ s}$, a maximum permissible drift $\alpha_{\max} = \Delta\vartheta_{\max} / \tau = 10 \text{ } \mu\text{K/s}$ may be derived from the second equation. This is a quantity statement which is valid for both positive and negative temperature changes. A maximum permissible temperature drift α_{\max} of $10 \text{ } \mu\text{K/s}$ of the water bath temperature ϑ_B may be

considered tolerable given the exemplary preconditions and does not lead to a controlled balancing. If the temperature drift α is only of short duration, the lag error would, of course, be smaller than .3 mK. At an exemplary maximum permissible lag error $\Delta\vartheta_{\max}$ of .1 mK and a time constant of 15 s the resultant value for a maximum permissible temperature drift α_{\max} would be about 7 $\mu\text{K/S}$.

After a time t_v following charging of the measuring cell with a sample liquid preheated for temperature equalization, the conductivity of the sample is measured. If during this time the temperature ϑ_B of the bath has increased by the maximum permissible drift α_{\max} , there will be a lag error

$$\Delta\vartheta_v = \alpha_{\max} \cdot T_v$$

between the bath and sample temperatures at the measuring time.

Hence, in pursuit of the first mentioned numeric example a maximum time interval $T_{v\max} = \Delta\vartheta_{\max} / \alpha_{\max}$ of 30 s will result between filling and measuring. This time can easily be adhered to. The error generated by this time lag is not added to the actual lag error; but it ought to be set to be smaller than the maximum permissible lag error.

20

III) Heat Currents

The heat current flowing in and out of the water bath are, in particular,

- the heat current P_K pumped from the water bath by cooling;
- 25 • the heat current P_H pumped into the water bath by heating;
- the heat current P_I generated by the difference in temperature $P_I = (\vartheta_B - \vartheta_L) / R_{WI}$ between the environment and the water bath and applied by the heat resistance of the water bath insulation;
- the heat current P_R input into the water bath by stirring;
- 30 • the heat current P_P input into the water bath by the sample which may be continually newly filled into the bath, if its temperature is different from the temperature of the water bath ($P_P = C_W V/t(\vartheta_P - \vartheta_B)$ ($V/t =$

mean volume current during filling);

- the heat current P_M input into the water bath by the electrical energy of the measuring sensor; and
- the heat current P_B input into the water bath by the illumination. It may generally be ignored.

A cover on top of the bath prevents the occurrence of heat currents from evaporation or condensation of room air humidity which would have additionally to be considered. The cooling power P_K is assumed to be constant at a constant flow through the cooling element even though its heat pumping ability depends somewhat from the temperature difference between the warm and the cold side. The heat current through the insulation of the bath container P_I is proportional to the temperature difference between its interior and the vicinity and thus amounts to one of the variable parameters, like the heat, which are input into the bath by samples of different temperature. They develop into a pulsating heat current by the uniform renewed filling of the measuring cell at the mean volume flow V/t . The temperature of the electrical power entering the bath as a result of the measuring sensors may be ignored.

Analogously to Ohm's law a heat resistance law describes the temperature difference $\Delta\vartheta$ over a heat resistor R_T through which a heat current is flowing as

$$\Delta\vartheta = R_T \cdot P_W$$

If a heat current P_W is flowing in a body of heat capacity C_W the temperature ϑ thereof will change as

$$d\vartheta/dt = P_W/C_W$$

The sum of the mentioned heat currents thus changes the temperature of the water bath to

$$d\vartheta_B/dt = 1/C_W(P_K + P_H + P_I + P_R + P_P + P_M)$$

IV) Heat resistance

The heat resistance of a Peltier element measuring 40 mm x 40 mm does not exceed 1 K/W. If the resistance of the insulation of the wall be 1.5 K/W, the total resistance thus is in the range of .6 K/W and can be increased to 1 K/W only regardless of the quality of the insulation of the wall. By contrast, the insulation of the Peltier element by a plate of PVC 3 mm thick and measuring 40 mm x 40 mm on the side of the bath, will raise its heat resistance to 7 K/W. The side facing the room will, however, be maintained at room temperature by a large cooling body and an intensive ventilator. The total heat resistance will then amount to 1.2 K/W. The additional insulation of the Peltier element will limited, however, the heat current pumped out of the bath to about 5 W because the temperature difference above the insulation plate amounts to $6 \text{ K/W} \cdot 5 \text{ W} = 30 \text{ K}$. If the temperature in the bath is 20°C the cold side of the Peltier element will be at -10°C whereas its warm side, because of the heat resistance of the cooling body, will be at about 25°C . In order to be able to pump a heat current of 5 W at a temperature difference of 35 K parallel operation of two or more Peltier elements may be required.

Embodiments of the invention will be described in greater detail with reference to the schematic drawings to provide an improved understanding of the method in accordance with the invention of determining the salinity of liquids and of an apparatus for practicing the method. In the drawings:

- Figure 1 depicts a flow diagram of the method in accordance with the invention;
- Figure 2 depicts an energy diagram for balancing a disturbance by the control parameter here termed "temperature drift" and for comparison with the known parameter "temperature"; and
- Figure 3 depicts a block diagram of an apparatus for practicing the method in accordance with the invention.

Figure 1 depicts the steps typical of the method in accordance with the invention as a flow diagram. Initially a standard calibration is performed with standard sea water SSW by the K_{15} -value. In its sequence the calibration flow corresponds to the measuring flow described infra. If the results of three salinity measurements are $S_{s1} = S_{s2} = S_{s3}$ the calibration will have been successfully concluded. Balancing of the bridge occurs automatically. A status report and the result are input into a PC. The form factor FF of the measuring cell MC and a possible calibration error KF of a utilized thermometer will be implicitly taken into consideration during calibration. As long as these measurement errors are small there compilation in a form factor is permissible.

In the ensuing measurement flow a sample PROBE is initially fed through a heatable and coolable advance bath PB to adjust the temperature ϑ_p to the temperature ϑ_b of the bath. Thereafter, it is conducted into a measuring cell MC arranged in a larger water bath WB. In the measuring cell MC the electrical conductivity κ is measured, and the value is input in the computer PC. Thereafter, the measuring cell MC is evacuated by pressurized air, cleaned by distilled water and filled with a new sample PROBE. The distribution of the flow of the individual media flows is carried out by a four-way valve FV controlled by the computer PC. The measuring flow may be continually repeated. New calibrations are periodically interjected at predetermined intervals.

During measurement of the electrical conductivity κ the temperature ϑ_b of the bath is continually measured, and the computer PC, with consideration of the time t between two measurements, calculates a temperature drift α on the basis thereof. In this connection it is assumed that the temperature ϑ_b of the bath is substantially identical, except for an arbitrarily determined small lag error $\Delta\vartheta$, to the temperature ϑ_p of the sample in the measuring cell MC. The size of the temperature drift α must be below a predetermined permissible maximum value α_{\max} to prevent the occurrence of a control

compensation (Regelausgleich). Shortly before reaching the permissible maximum value α_{\max} of the temperature drift a mean heat current P_{Hm} (including the kinetic stirring power P_R) is automatically altered to a residual heat current P_{rest} by a stirring propeller Q for balancing the entire heat
5 currents P_{ges} including the heat current from the vicinity P_l and a cooling power P_K . The residual heat current P_{rest} must not exceed a predetermined maximum residual heat current P_{restmax} . Otherwise the control will intervene.

Thus, the control parameter is constituted by the temperature drift α
10 which is set in relation to the maximum permissible temperature drift α_{\max} . The maximum permissible temperature drift α_{\max} is calculated as quotient from the predetermined maximum permissible lag error $\Delta\vartheta_{\max}$ between the bath and sample temperatures ϑ_B , ϑ_P and the time constants τ ($\alpha_{\max} = \Delta\vartheta_{\max}/\tau$). The control value in the control circuit is the heating power P_H input
15 into the water bath WB by the stirring propeller Q, and the disturbance value is the sum of all occurring heat currents P_{ges} .

The salinity S of the sample PROBE is finally calculated on the basis of the measured values of the temperature ϑ_B of the water bath WB and of the
20 conductivity κ of the filled sample PROBE by a calculation program used in oceanography on the basis of the UNESCO formula. The calculated value and the disturbances in the process sequence are rendered optically visual.

From Figure 2 depicts an energy diagram related to given control
25 operations. In order to show an optimum energy balance (at the bottom of the Figure) by practicing the method according to the invention with the LRM, the energy balance of the known method practiced with the AS 8400 is also depicted (at the top of the Figure) for reasons of comparison. The heat currents into the water bath and the heat currents out of the water bath have
30 been depicted as surfaces up to a limit curve, above a time line t. At points in time t_{x1} and t_{x2} abrupt significant disturbances occur as a result of heat currents P_l from the vicinity and which require controlled compensation. For

instance, at time t_{x1} a person being a heat source may approach the water bath, at point t_{x2} a door may be opened and heat may escape from the room. In both control methods the cooling power is always constant. In the AS 8400 the stirring power P_R is also constant, and additional heating energy P_H occurs. It is generated by digitally controlled heat lamps. In the LRM the disturbance is compensated by the heating power P_H being augmented by the stirring power P_R as a result of controlling the rotations of the stirring propeller Q . The sawtooth curve of the temperature ϑ_B of the water bath may be clearly seen with the AS 8400, the curve being intended to maintain as a control parameter a constant temperature ϑ_B of the water bath. By contrast, the temperature ϑ_B of the water bath of the LRM depicts a substantially continuous curve. As long as the temperature drift α does not exceed its permissible maximum value further adjustment of the stirring power P_R is not necessary. The known complex maintenance of a constant bath temperature ϑ_B has become unnecessary with the LRM. At the depicted point in time for calibrations K_{t1} , K_{t7} and measurements $M_{t2}..M_{t6}$ it can be clearly seen how much the water bath and sample temperatures ϑ_B , ϑ_p may deviate in the prior art from the implicitly assumed temperature, whereas in the method according to the invention it is measured each time except for the maximum permissible lag error $\Delta\vartheta_{max}$ and is integrated into the calculation of the salinity S . The much greater accuracy of the measurements yielded thereby is obvious.

Figure 3 depicts a conductivity-reference-measuring site LRM as a preferred arrangement for practicing the method according to the invention. The LRM is provided with a water bath WB and a separate advance bath PB. In the advance bath PB which may be heated as well as cooled by a Peltier element there is provided a preheat exchanger PWT for temperature adjustment between a sample PROBE taken from a sample bottle B (or standard sea water SSW from a vial A for calibration) and the water bath WB. In the water bath WB a measuring cell MC is positioned behind a main heat exchanger WT. The measuring cell is provided with four strip electrodes SE for measuring the changing values of current and voltage. Almost all media

flows are fed by a dosage pump DP and flow through hoses T by way of a four-way valve FV acting as a distributor. Pressurized air required for evacuating the measuring cell MC is generated by a diaphragm pump MP as needed and is fed into the measuring cell MC by way of a two-way valve TV.

- 5 The electrical conductivity κ is measured in the measuring cell MC at a fully automatically balancing precision bridge (not shown) by means of a computer PC. Furthermore, there are provided in the water bath WB a precision thermometer TM for measuring the temperature ϑ_b of the water bath and a rotation-controlled stirring propeller Q with a propeller SP similar to a ship's
- 10 screw for controlling the temperature drift α by way of the mean input heating power P_{hm} . In the embodiment shown, it is the commercially available thermometer "SBE3plus" of the "Seabird" company, which because of its stability drifts less than 1 mK during the course of a year and which satisfied the requirements without any problems. The stirring propeller Q is provided
- 15 with an electric motor EM arranged outside of the water bath and counteracts a continually cooling Peltier element PE which for increasing its heat resistance R is provided with an insulation I similar to the water bath WB.

In the selected embodiment the stirring propeller Q has an operating

20 range between 3 W and 5 W and, hence, a working point at 4 W. Considering the relationship between temperature and heat current ($d\vartheta/dt = P/C_W$) and the predetermined limit and material values the heat current balance may be balanced with ± 1 W. If .5 W is reserved for the heat current of the ambient temperature ϑ_L may now deviate from the water bath

25 temperature ϑ_b by 1 K without the temperature drift α taking on impermissibly high values. At these values, the total resulting heat resistance is 2 K/W. If the resistance of the insulation I of Peltier element PE and heat exchanger WT is 7 K/W the insulation of the bath must be 2.8 K/W. To this end the resistance value may, if necessary, have to be increased.

30

From the relationship mentioned supra it is possible with the maximum permissible temperature drift $\alpha_{max} = d\vartheta/dt$ as default and knowing the resulting

heat capacity C_{WB} of the water bath WB ($V_W \cdot C_{WS}$) to calculate the tolerable residual error of the heat current P_{rest} to be balanced. For instance, $\alpha_{max} = 7$ $\mu K/s$ and $C_{WB} = 67 \cdot 10^3$ Ws/K for a water bath of a volume $V_W = 16$ l and a specific C_{WS} value for water of $4.2 \cdot 10^3$ $Ws/(1K)$ result in a power of $P_{rest} = .47$

- 5 W. At an improved heat resistance $R_{WI} = 1.2$ K/W of the water bath according to the equation $\Delta\vartheta = R \cdot P$ the ambient temperature ϑ_L may now deviate from the bath temperature ϑ_B by .56 K without the control having to intervene.

List of formulas and reference characters

10

A	vial
B	sample bottle
C_{WB}	heat capacity of the water bath
C_W	heat capacity
15 C_{WS}	specific heat capacity
DP	dosage pump
EM	electric motor
FF	form factor
I	insulation

20

K_{15}	standard value
KF	calibration error
$K_{t1/2}$	calibration points in time
LRM	conductivity reference site
$M_{t2...6}$	measuring time points

25

MC	measuring cell
MP	diaphragm pump
PB	advance bath
PC	personal computer
PE	Peltier element

30

P_{ges}	total heat current
P_H	heating power
P_{Hm}	mean heating current

	P_l	heat current from the vicinity
	P_k	cooling power
	P_p	heat flow through the sample
	P_R	kinetic stirring power
5	P_{rest}	residual heat current
	$P_{restmax}$	maximum residual heat current
	P_W	heat current
	PROBE	liquid sample
	PWT	advance heat exchanger
10	Q	stirring propeller
	R	heat resistance
	S	salinity
	$S_{s1, s2, s3}$	individual measurement
	SE	strip electrode
15	SP	ship's screw propeller
	SSW	standard sea water
	t	time
	T	hose
	TM	thermometer
20	t_v	time interval for filling/measuring
	TV	two-way valve
	WB	water bath
	WT	heat exchanger
25	ϑ_p	temperature of sample
	ϑ_B	temperature of bath
	$\Delta\vartheta_{max}$	maximum permissible measurement error
	α	temperature drift
	α_{max}	maximum permissible temperature drift
30	κ	electrical conductivity
	T	time constant of the measuring cell

Patent Claims

1. Method of determining the salinity of liquids by standard calibrated measurements of the electrical conductivity of a heated liquid sample in a measuring cell arranged in a constantly cooled and mechanically stirred as well as heatable water bath which is insulated to the exterior under control parametric consideration of the thermal conditions in the water bath characterized by the fact that the actual temperature (ϑ_B) is measured as an equivalent of the temperature (ϑ_P) of the sample with a high repetitive accuracy and inclusion of a maximum permissible lag error ($\Delta\vartheta_{\max}$) between the water bath and sample temperature (ϑ_B , ϑ_P) set by the required accuracy of determining the salinity (S), and that the control parameter for taking into account the thermal conditions is the time-wise drift ($\alpha = \Delta\vartheta_B/t$) of the temperature (ϑ_B) derivable from the temperature measurements, the permissible maximum value (α_{\max}) of which is defined as quotient ($\alpha_{\max} = \Delta\vartheta_{\max}/\tau$) of the maximum permissible lag error ($\Delta\vartheta_{\max}$) and a time constant (τ) of the measuring cell (MC) for a temperature equalization between the interior of the measuring cell and the water bath (WB), whereby the permissible maximum value of the time-wise drift (α_{\max}) of the temperature (ϑ_B) of the water bath is maintained by a low-lag and quickly controllable compensation of the heat currents (P_{\pm}) flowing into and out of the water bath (WB) to such a degree that the resulting quantity of the residual heat current (P_{rest}) does not exceed a predetermined maximum value (P_{restmax}).

25

2. Measuring method of claim 1, characterized by the fact that the temperature (ϑ_B) of the water bath is maintained with the resultant residual heat current (P_{rest}) at the mean ambient temperature approximately

with a deviation of ± 1 K.

3. Measuring method according to claim 1 or 2,
characterized by the fact that

5 the energy input into the water bath (WB) by the stirring (P_R) is also utilized
for the quick and low-lag controllable heating (P_H) thereof.

4. Measuring method according to at least one of claims 1 to 3,
characterized by the fact that

10 the heat resistance (R) of the exterior insulation (I) of the water bath (WB) is
high.

5. Measuring method according to at least one of claims 1 to 4,
characterized by the fact that

15 the heat resistance (R) of the water bath cooling (PE) on the side of the bath
is high.

6. Measuring method according to at least one of claims 1 to 5,
characterized by the fact that

20 that the temperature of the liquid sample (ϑ_P) is adjusted to the temperature
(ϑ_B) of the water bath in a separately controlled advance bath (PB).

7. Measuring method according to at least one of claims 1 to 6
characterized by the fact that

25 the measuring sequence is carried out automatically by a computer (PC) and
that the salinity (S) of the liquid sample (PROBE) is calculated from the
measured values of temperature (ϑ_B) and conductivity (κ) on the basis of the
UNESCO formula.

30 8. Apparatus for practicing the method according to at least one of claims
1 to 8 of determining the salinity of liquids by standard calibrated

measurements of the electrical conductivity of a heated liquid sample which may be transferred from a sample vial into a measuring cell arranged in a water bath provided with a cooling, a stirring and a heating element as well as with a heat exchanger and provided at its wall with an external insulation and

5 a control device in which the actual temperature (ϑ_b) of the water bath is measured with high repetitive accuracy and including a maximum permissible lag error ($\Delta\vartheta_{\max}$) between the water bath and sample temperature (ϑ_b , ϑ_p) determined by the accuracy demanded in by the determination of salinity (S) as the equivalent of the temperature (ϑ_p) of the sample and wherein the

10 control parameter for taking into account the thermal conditions is the time-wise drift ($\alpha = \Delta\vartheta_b/t$) of the temperature (ϑ_b) of the water bath the permissible maximum value (α_{\max}) of which is defined as quotient ($\alpha = \Delta\vartheta_{\max}/T$) of the maximum permissible lag error ($\Delta\vartheta_{\max}$) and a time constant (τ) of the measuring cell (MC) for a temperature balancing between the interior of the

15 measuring cell and the water bath (WB), whereby the permissible maximum value of the time-wise drift (α_{\max}) of the temperature (ϑ_b) of the water bath is maintained to such a degree by a low-lag and quick controllable adjustment of the heat currents (P_{\pm}) flowing into and out of the water bath (WB) that the quantity of the resulting residual heat current (P_{rest}) does not exceed a

20 corresponding predetermined maximum value (P_{restmax}), whereby for the direct measurement of the actual temperature ($\Delta\vartheta_b$) of the water bath there is provided in the water bath a precision thermometer (TM) having a long term stability of less than 1 K per year and a time constant of less the .5 s.

25 9. Measuring apparatus of claim 8, characterized by the fact that the precision thermometer (TM) is provided with temperature dependent semiconductor resistors.

30 10. Measuring apparatus according to claim 8 or 9, characterized by the fact that

the stirrer provided for stirring and heating the water bath (WB) is structured as a rotationally controllable stirring propeller (Q) having a stirring vane (SP) similar to a ship's screw of high hydrodynamic efficiency which is drivable by a continuously controllable electric motor (EM) arranged at the exterior of the
5 water bath (WB).

11. Measuring apparatus according to at least one of claims 8 to 10, characterized by the fact that
that in the wall of the water bath (WB) there is arranged at least one Peltier
10 element (PE) provided with a thermal insulation (I) at the cooling side of the water bath (WB).

12. Measuring apparatus according to at least one of claims 8 to 11, characterized by the fact that
15 the measuring cell (MC) has a volume in the range of 2 ml and is provided with strip electrodes (SE).

13. Measuring apparatus according to at least one of claims 8 to 12, characterized by the fact that
20 that for heating the liquid sample (PROBE) there is provided a separate controllable advance bath (PB) provided with a preheat exchanger (PWT).

14. Measuring apparatus according to at least one of claims 8 to 13, characterized by the fact that
25 for carrying out standard calibrations and measurements there is provided a four-way valve (FV) provided with inputs to a vial (A) of standard sea water (SSW), to a bottle (B) of sample water (PROBE) as well as to a cleaning and an air conduit (H₂O, Air).

30 15. Measuring apparatus according to at least one of claims 8 to 14, characterized by the fact that

for evacuating the measuring cell (MC) there is provided a diaphragm pump (MP).

16. Measuring apparatus according to at least one of claims 8 to 15,
5 characterized by the fact that
for filling the measuring cell (MC) there is provided a dosage pump (DP).

17. Measuring apparatus according to at least one of claims 8 to 16,
characterized by the fact that
10 a computer (PC) is provided for regulating the water bath, controlling the
measuring sequence, and storing results.

18. Measuring apparatus according to at least one of claims 8 to 17,
characterized by the fact that
15 that the conductivity measurement of the liquid sample (PROBE) is carried
out at a fully automatically balancing precision bridge.

19. Measuring apparatus according to at least one of claims 8 to 18,
characterized by the fact that
20 there is provided an indicator of satisfied measuring conditions.

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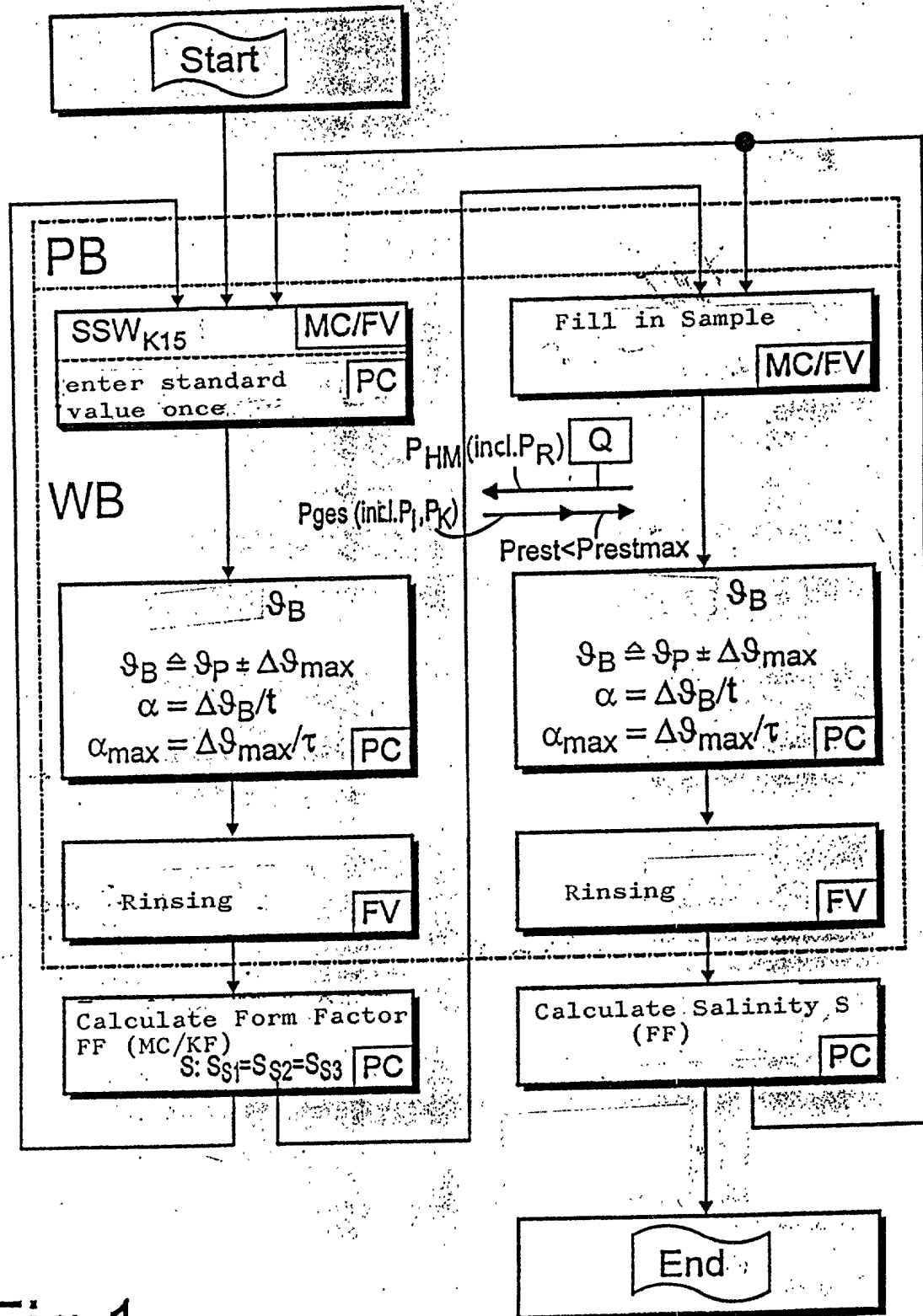


Fig.1

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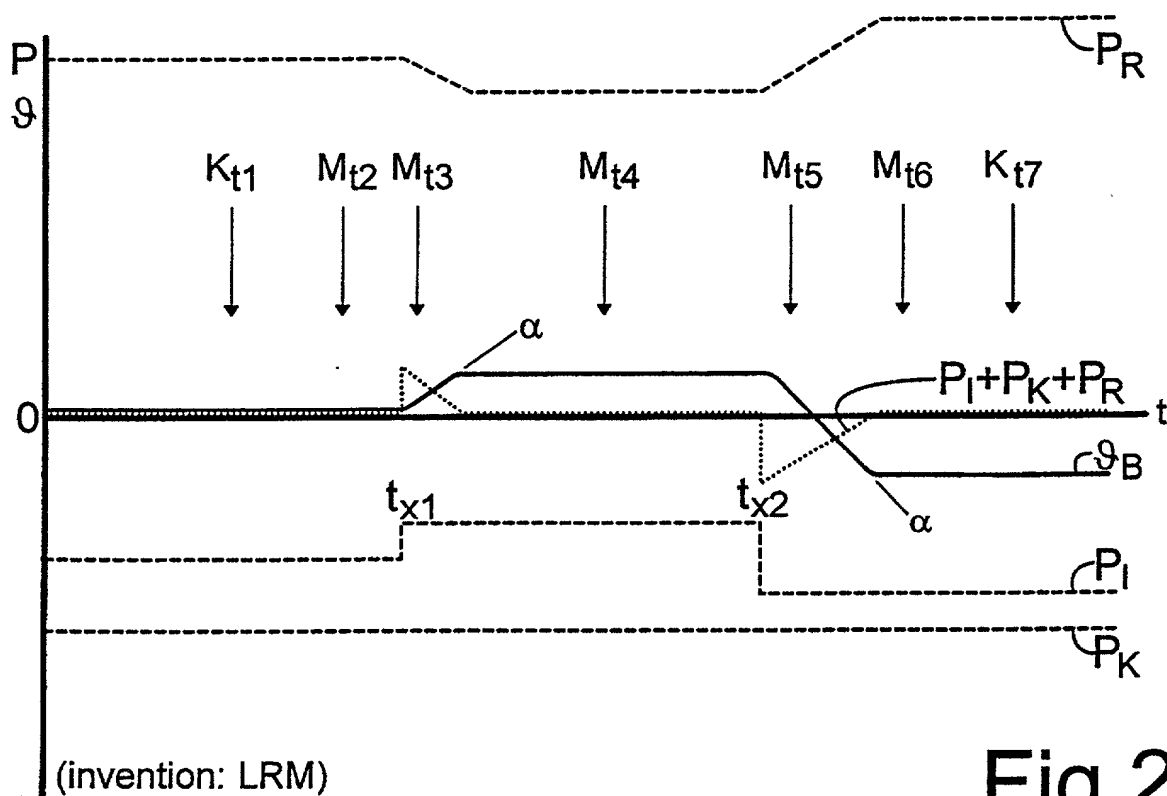
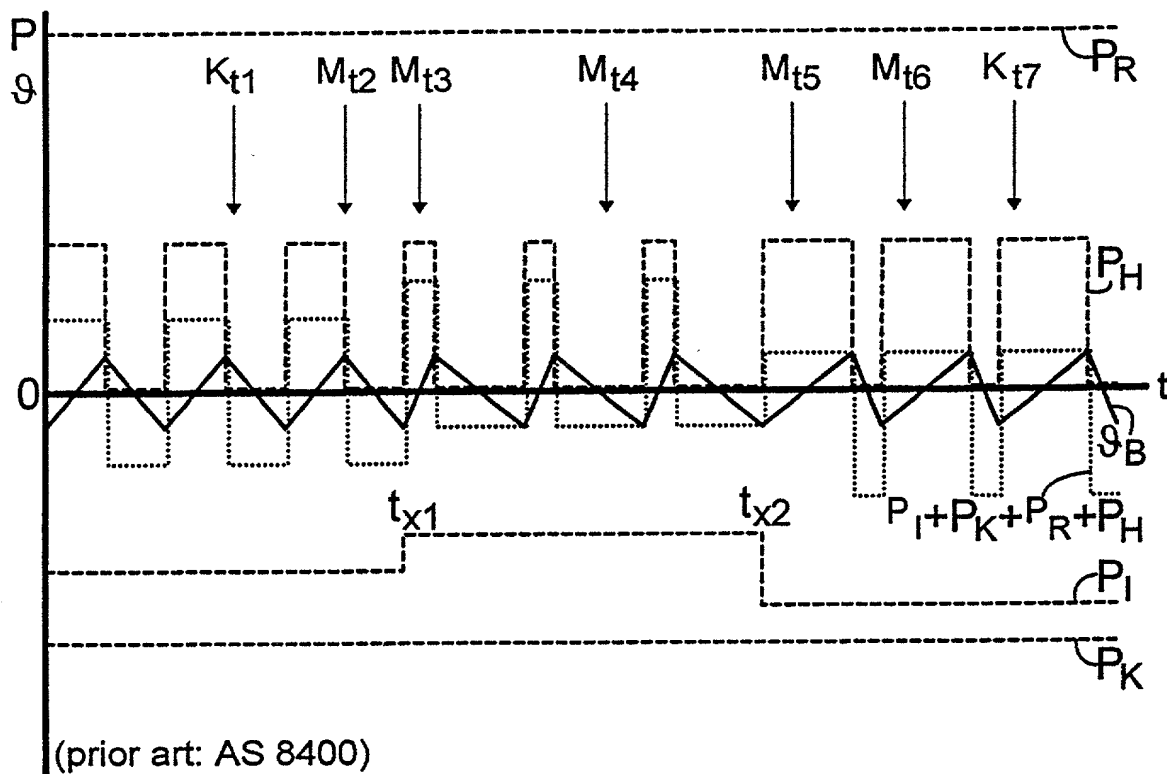


Fig.2

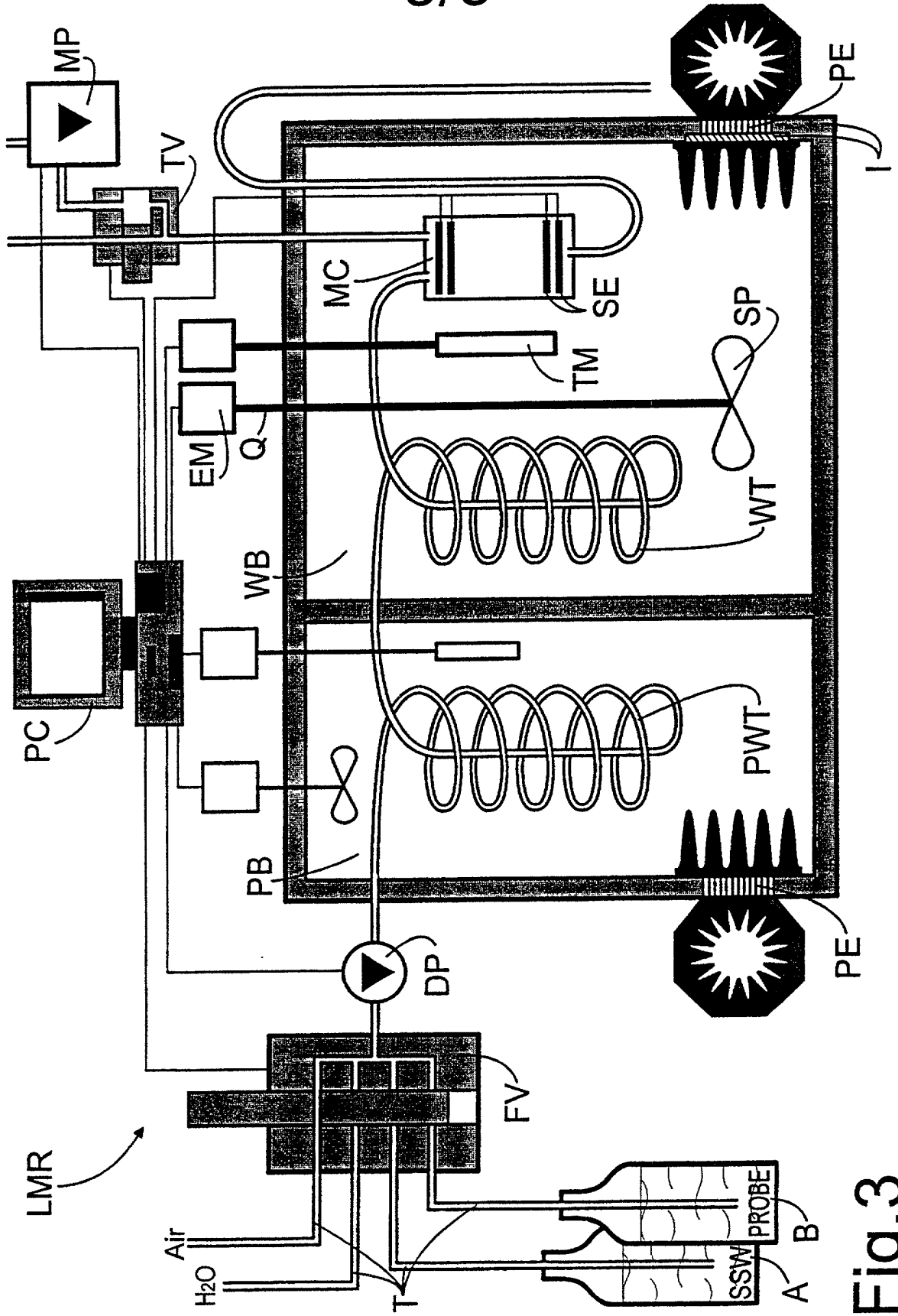


Fig.3

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional

N/A

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(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

PCT/DE00/01313

26 April 2000

Pending

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

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